

# PATENT SPECIFICATION

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## (54) DETERGENT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, 45202 Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to antistatic and softening detergent compositions containing water soluble ortho and pyrophosphates as detergency builders. More particularly it relates to the provision of simultaneous antistatic, softening and cleaning benefits from a detergent composition containing low amounts of phosphorous based builders.

For many years the primary detergency builder used to control water hardness in detergent products has been sodium tripolyphosphate, used at high levels, for instance usually from about 30 to 60% of the product. Within the past few years competition for other uses of phosphate has made STPP increasingly expensive and variable in supply for detergents; and the use of high levels of phosphates has come under scrutiny because of the suspicion that the soluble phosphates accelerate the eutrophication of natural waters such as rivers and lakes.

As more fully explained in German Offenlegenschrift 2,605,052 and 2,542,704, ortho- and pyrophosphates can remove more hardness ions ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ) per unit of  $\text{P}_2\text{O}_5$  in their constitution than can tripolyphosphate. They do so, however, by precipitating these ions mainly as insoluble phosphates whereas sodium tripolyphosphate retains them in solution as complex ions. Unless special precautions are taken, for instance, those taught in said Offenlegenschrift these precipitates cause undesirable effects upon fabrics, such as greyness or harshness of feel. Clearly, by overcoming these faults, and other faults of the compositions, a very valuable saving in usage and cost of phosphate and reductions in the amount entering natural waters can be achieved.

Although, as has just been stated, these said inventions have gone some way to overcome the objectionable deposition upon fabrics particularly, in low conditions of low product concentration, wash temperature and load-to-liquor ratios, the compositions described still cause some deposits upon the drums of washing machines and more especially upon their heating elements. German Offenlegenschrift 2,650,281 describes improvements in such compositions particularly under conditions of high product concentration, wash temperature and load-to-liquor ratio, wherein deposition upon the inner surfaces of washing machines is almost eliminated and the amount of deposition upon fabrics is reduced.

The present invention provides a further reduction in the greyness/harshness side effects resulting from the use of ortho- and pyrophosphate builders by the inclusion of a low level of a selected quaternary ammonium material in the built detergent composition. Surprisingly, it has been found that the level of softening benefit provided by the quaternary ammonium material in this system is sufficient not only to counteract the harshness negatives of the ortho and pyrophosphate builders, but also to provide a positive softness improvement which can match or exceed that obtained in a conventional tripolyphosphate-built composition. Moreover this advantage is obtained essentially without detriment to the cleaning performance of the composition or to its fabric ash deposition performance.

Thus, according to the present invention, there is provided a built detergent composition comprising by weight:

(a) from 1% to 70% of an organic surfactant selected from anionic, nonionic, zwitterionic surfactants, and mixtures thereof,

(b) from 5% to 50% of a mixture of water soluble ortho and pyrophosphate salts, the weight ratio of ortho to pyrophosphate salts being in the range from 9:2 to 3:7,

(c) from 0.5% to 25% of one or more quaternary ammonium compounds of formula  $(R_1R_2R_3R_4N)^+Y^-$ , wherein at least one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is an organic radical containing a group selected from a  $C_{16}$ — $C_{22}$  aliphatic radical, or an alkyl phenyl or alkyl benzyl radical having 10 to 16 carbon atoms in the alkyl chain, the remaining group or groups being selected from  $C_1$ — $C_4$  alkyl,  $C_2$ — $C_4$  hydroxyalkyl, and cyclic structures in which the nitrogen atom forms part of the ring, and  $Y$  constitutes an anionic radical, e.g. halide or methyl-sulphate.

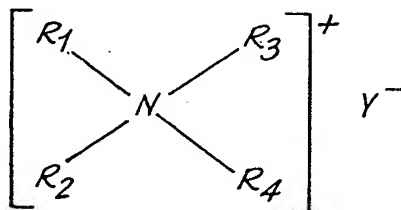
In a preferred aspect of the invention, the selected quaternary ammonium compounds are used in combination with a polycarboxylate material of the type described in German Offenlegungsschrift 2,650,281 or with a  $C_8$  to  $C_{24}$  fatty acid soap, or with a mixture of the two. These adjuvants are found to enhance the effectiveness of the quaternary ammonium compound in reducing the harshness and greyness effects resulting from mixed ortho- and pyrophosphate salt builders.

The various essential and preferred components of the compositions of the invention will now be discussed in detail.

#### Antistatic Agent

The built laundry detergent composition of the invention preferably comprises from 1% to 25% of a particulate combination comprising an intimate mixture consisting essentially of

A) from 80% to 20% by weight of a quaternary ammonium antistatic agent of the formula:—



wherein  $R_1$  and preferably also  $R_2$  represent an organic radical containing a group selected from a  $C_{16}$ — $C_{22}$  aliphatic radical or an alkyl phenyl or alkyl benzyl radical having 10—16 atoms in the alkyl chain,  $R_3$  and  $R_4$  represent hydrocarbyl groups containing from 1 to 4 carbon atoms and wherein  $Y$  is an anion, e.g. fluoride, chloride, bromide, or methylsulfate; and

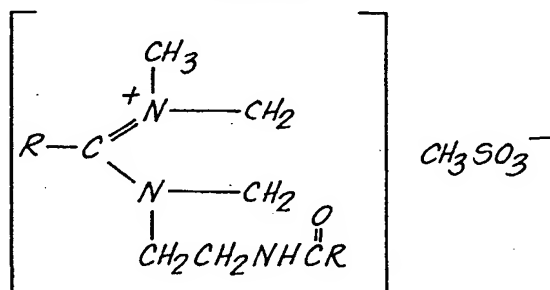
B) from 20% to 80% of a solid organic dispersion inhibitor having a softening point in the range of from 100°F to 200°F and a solubility in water of 50 ppm max at 25°C, selected from the group consisting of paraffinic waxes, cyclic and acyclic mono- and polyhydric alcohols, substituted and unsubstituted aliphatic carboxylic acids, esters of the foregoing alcohols and acids,  $C_3$ — $C_4$  alkylene oxide condensates of any of the foregoing materials and mixtures thereof, the individual particles having a size in the range of 10 $\mu$  to 500 $\mu$ , a solubility in water of 50 ppm max at 25°C and a softening point in the range of 100°F to 200°F.

The particulate combination of quaternary ammonium compound and dispersion inhibitor are described in detail in German Offenlegenschrift 2,548,242 incorporated herein by reference.

The quaternary ammonium antistatic agent will normally be present in the detergent compositions of the invention in an amount of from 0.5% to 15% preferably in an amount of from 1% to 10% and most preferably in an amount of from 2% to 5% by weight of the composition. Generally, an amount of detergent sufficient to provide a concentration of quaternary ammonium compound in the bath or liquor of from 5 ppm (parts per million) to 500 ppm is employed.

In the context of the above definition of the quaternary ammonium compound, the hydrophobic moiety (i.e. the  $C_{16}$ — $C_{22}$  aliphatic,  $C_{10}$ — $C_{18}$  alkyl phenyl or alkyl benzyl radical) in the organic radical  $R_1$  may be directly attached to the quaternary nitrogen atom or may be indirectly attached thereto through, for example, an amide, ester, alkoxy, or ether grouping.

The quaternary ammonium antistatic compounds useful herein include both water soluble and substantially water insoluble materials. For example, the imidazolinium compounds of the structure



where R is a C<sub>16</sub>—C<sub>20</sub> alkyl group, possess appreciable water solubility but can be utilized in the present invention by mixture with the appropriate level and type of organic dispersion inhibitor so as to give an ultimate particle solubility in water of less than 50 ppm at 25°C.

Similarly, other relatively water-soluble quaternary ammonium antistatic agents can be used such as the diisostearyl dimethyl ammonium chlorides disclosed in U.S. Patent 3,395,100 to Fisher et al.

However, the preferred quaternary ammonium antistatic agents useful herein are characterized by their limited solubility in water. That is to say, such quaternary salts are essentially insoluble in water, existing therein in what appears to be the mesomorphic liquid crystalline state.

The quaternary ammonium antistatic agents used in this invention can be prepared in various ways well known in the art. Many such materials are commercially available. The quaternaries are often made from alkyl halide mixtures corresponding to the mixed alkyl chain lengths in fatty acids. For example, the "di-tallow" quaternaries are made from alkyl halides having mixed C<sub>14</sub>—C<sub>18</sub> chain lengths. Such mixed di-long chain quaternaries are useful herein and are preferred from a cost standpoint.

The organic dispersion inhibitor generally comprises 20% to 80%, preferably from 20% to 50%, and most preferably 20% to 30% by weight of the particulate combination and is present in an amount from 0.5% to 15%, preferably from 1% to 10% by weight of the total composition. Normally, an amount of dispersion inhibitor sufficient to provide a weight ratio of quaternary ammonium compound to dispersion inhibitor of from 4:1 to 1:1, and preferably from 2:1 to 7:2 and especially about 3:1 is employed.

The dispersion inhibitor has a solubility in water of 50 ppm max at 25°C and a softening point in the range of 100°F—200°F, preferably 125°F—200°F, and is selected from the group consisting of paraffinic waxes, cyclic and acyclic mono- and polyhydric alcohols, substituted and unsubstituted aliphatic carboxylic acids, esters of the foregoing alcohols and acids, C<sub>3</sub>—C<sub>4</sub> alkylene oxide condensates of any of the foregoing materials and mixtures thereof.

Preferred herein because of ready availability is tallow alcohol, but useful dispersion inhibitors include other fatty alcohols in the C<sub>14</sub>—C<sub>26</sub> range such as myristyl alcohol, cetyl alcohol, stearyl alcohol, arachidyl alcohol, behenyl alcohol, and mixtures thereof.

Saturated fatty acids having 12 to 24 carbon atoms in the alkyl chain can be used such as: lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, and behenic acid, as well as mixtures of these, particularly those derived from naturally occurring sources such as tallow, coconut, and marine oils.

Esters of the aliphatic alcohols and fatty acids are useful dispersion inhibitors, provided they have a total of more than 22 carbon atoms in the acid and alkyl radicals. A preferred material of this type is sold under the trade name "Castorwax".

Long chain C<sub>22</sub>—C<sub>30</sub> paraffinic hydrocarbon materials such as the saturated hydrocarbon octacosane having 28 carbon atoms can also be used.

Another preferred class of materials useful in the present invention are the water insoluble sorbitan esters which comprise the reaction product of C<sub>12</sub>—C<sub>28</sub> fatty acyl halides or fatty acids and the complex mixtures of cyclic anhydrides of sorbitol collectively known as "sorbitan".

Materials of this general class are commercially available under various trade names, e.g., the Span (trade mark) series sold by Atlas Chemical Corporation.

### The Builder

The essential builder components are water-soluble ortho- and pyrophosphate salts. In solid compositions the sodium salts are preferred, in liquids the more soluble potassium or alkanol-ammonium salts may be more suitable. It is important that both ortho- and pyrophosphate be present in the stated proportions. Preferred weight ratios of ortho- to pyrophosphate are within the ranges from 4:1 to 2:3, especially from 7:3 to 1:1 and desirably from 65:35 to 55:45. The total content of ortho- and pyrophosphate together in the compositions is preferably from 5% to 45%, more preferably from 10% to 35%, and most preferably from 15% to 35% by weight. If the proportion of pyrophosphate is too low, cleaning (soil removal) performance of the products begins to deteriorate.

The compositions of the invention may contain other inorganic or organic salts and compounds which have detergency building action; many such substances are known. The compositions may contain other salts or hydroxides which serve to provide necessary alkalinity as more fully described below.

Thus the use of additional phosphates which are more condensed than pyrophosphates (for example sodium tripolyphosphate, or still more condensed phosphates such as glassy metaphosphates as disclosed in German Offenlegungsschrift 2,606,684) does not normally impair the washing performance of the compositions and can indeed be beneficial. Their use does, of course, reduce the economy in phosphate usage achieved by the compositions, and it is preferred that the total amount of tripolyphosphate and still more condensed phosphates should not form more than 25% by weight of the total phosphates in the composition, and that any glassy metaphosphates should not form more than 4% by weight of the total compositions.

Other inorganic salts which have some detergency building effect and effect upon the alkalinity of the compositions include sodium or potassium carbonates, aluminates, borates, sulphates and silicates. Yet other inorganic builders are the insoluble zeolites or aluminosilicates, which are described in Irish Published Patent Application 1505/74 and Belgian Patent 814,874. The latter can be present, if at all, in an amount from 1 to 40%, preferably 5 to 25%, by weight of the composition.

Examples of suitable organic detergency builders are given in German Offenlegungsschrift 2,605,052. Representative classes of such organic builders include water soluble aminopolycarboxylates, phytates, polyphosphonates, polymeric aliphatic polycarboxylates, polyacetates, ether polycarboxylates and citrates.

Preferably the compositions of the present invention have a level of free alkalinity that provides a pH in use of between 9.0 and 10.5, preferably between 10.0 and 10.5. This free alkalinity is measured and defined by the following test.

A solution of 10 g of the total composition in 990 g of water is prepared and its pH is measured, and must be above 9.5. The solution is then titrated with 0.1 N hydrochloric acid until the pH is reduced to and remains steady at 9.5. The sodium hydroxide (NaOH) equivalent to the added acid, expressed as a weight percentage of the composition, represents its free alkalinity.

The desirable free alkalinity in the compositions can be obtained by selection of the more highly alkaline of the builder or other salts, e.g. trisodium orthophosphate, sodium carbonate, sodium metasilicate, or by simply adding alkali, such as sodium or potassium hydroxide, for instance in preparing the slurry (crutcher mix) for spray drying to form granular products.

In solid, granular or particulate compositions it is preferred that the alkalinity is engendered by the use of sodium silicate. This can have  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio (molar) from 1:1 to 4:1, the preferred ratio being from 1.6:1 to 3.2:1, which ratios tend to give the most satisfactory spray drying behaviour and granule properties.

### The Detergent

From 1% to 70% by weight, preferably 2% to 25% by weight and most preferably from 5% to 20% by weight, of the detergent compositions can comprise an organic surfactant selected from anionic, nonionic, zwitterionic detergents and mixtures thereof. Examples of organic surfactants of these types are described in U.S. Patent 3,852,211 incorporated herein by reference.

Water soluble salts of the higher fatty acids, i.e. "soaps" are useful as the anionic surfactant herein. This class of surfactants includes ordinary alkali metal soaps such as the sodium, potassium, ammonium, and alkanolammonium salts of higher fatty acids containing from 8 to 24 carbon atoms and preferably from 10 to 20 carbon atoms. Soaps can be made by direct saponification of fats and oils or by

the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e. sodium or potassium tallow and coconut soaps.

Another class of anionic surfactant includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 8 to 22 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of surfactants which can be used in the present invention are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (8 to 18 carbon atoms) produced by reducing the glycerides of tallow or coconut oil; olefin sulphonates of from 8 to 24 carbon atoms described, for example, in US Patent 3,332,880; and alkali metal alkyl glyceryl ether sulphonates, especially those ethers of the higher alcohols derived from tallow and coconut oil. Other anionic detergents include the sodium and potassium alkyl-benzene sulphonates, in which the alkyl group contains from 9 to 15 carbon atoms, including those of the types described in United States Patents Nos. 2,220,099 and 2,477,383 (the alkyl radical can be a straight or branched aliphatic chain); sodium coconut oil fatty acid monoglyceride sulphates and sulphonates, salts of alkyl phenol ethylene oxide ether sulphates with 1 to 12 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 18 carbon atoms; the reaction product of fatty acids esterified with isethionic and neutralised with monoethanolamine where, for example, the fatty acid is oleic or derived from coconut oil; sodium or potassium salts of fatty acid amines of a methyl tauride in which the fatty acids, for examples, are derived from coconut oil; sodium or potassium  $\beta$ -acetoxy- or  $\beta$ -acetamido-alkanesulphonates where the alkane has from 8 to 22 carbon atoms; and other known in the art. A number are specifically set forth in United States Patents Nos. 2,486,921; 2,486,922; and 2,396,278.

Other synthetic anionic detergents useful herein include alkyl ether sulphates. These materials have the formula  $RO(C_2H_4O)_xSO_3M$  wherein R is alkyl or alkenyl of about 8 to 24 carbon atoms, x is 1 to 30, and M is a salt-forming cation selected from alkali metal, ammonium and substituted ammonium, e.g. trimethyl-, triethyl-, dimethanol-, diethanol-, trimethanol- and triethanol ammonium cations.

The alkyl ether sulphates are condensation products of ethylene oxide and monohydric alcohols having 8 to 24 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g. coconut oil or tallow, or can be synthetic. Lauryl alcohols and straight-chain alcohols derived from tallow are preferred herein.

Such alcohols are reacted with from 1 to 12, preferably 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 6 moles of ethylene oxide per mole of alcohol, is sulphated and neutralized.

The preferred nonionic surfactant is a polyalkoxy nonionic surfactant produced by the condensation of alkylene oxide groups with an organic hydrophobic aliphatic alcohol or alkylphenol. The polyoxyalkylene radical forms the hydrophilic portion of the surfactant and its length can be readily adjusted to yield a nonionic surfactant having any desired degree of balance between hydrophilic and hydrophobic properties.

In more specific terms, the nonionic surfactant component can be chosen from.

1. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight-chain or branched-chain configuration, with from 1 to 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent pretreatment and through-the-wash detergency performance on fatty and greasy soils.

However, it will be understood that the invention, in its broadest aspects, is equally applicable to nonionic surfactants having longer alkyl and/or alkoxy chain lengths, or indeed to combinations of two or more nonionic surfactants as disclosed generally in German Offenlegungsschrift 2,448,532 and 2,511,677.

The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the

Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell Chemical Co. and Shell International Chemicals Ltd. respectively), or Synperionics, which have about 50% 2-methyl branching (Synperonic is a trade name of Imperial Chemical Industries Ltd.) or the primary alcohols having more than 55% branched chain structure disclosed generally in Belgian Patent No. 850,016. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohols with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms.

Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol (trade mark) series having from 9 to 16 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule. The Tergitols are supplied by Union Carbide Chemicals Co.

2. The polyethylene oxide condensates of alkyl phenol, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight-chain or branched-chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerised propylene, di-isobutylene, octene or nonene.

Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol, nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

4. The compounds formed by condensing ethylene oxide with a  $C_8$  to  $C_{13}$  fatty acyl group.

Of the above, the preferred classes of surfactant are 1 and 2.

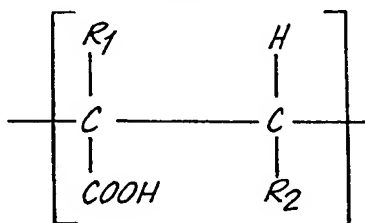
Preferred zwitterionic materials are derivatives of quaternary ammonium compounds containing an aliphatic straight chain group of 14—18 carbon atoms and a sulfate or sulfonate anionic solubilizing group. Specific examples include 3 - (N,N - dimethyl - N - hexadecyl ammonio - 2 - hydroxypropane - 1 - sulfonate; 3 - (N,N - dimethyl - N - tetradecyl ammonio) propane - 1 - sulfonate; and 6 - (N,N - dimethyl - N - hexadecylammonio) hexanoate.

Of all the above, a particularly useful detergent mixture, from the point of view of enhancing the fabric harshness/greyness inhibiting benefits of the composition of the invention, comprises from 1% to 20% of a  $C_8$  to  $C_{24}$  fatty acid salt such that the quaternary ammonium compound and the fatty acid salt are present in a weight ratio of from 20:1 to 1:30, more preferably from 5:1 to 1:10 and especially from 1:1 to 1:5. In such compositions, an auxiliary anionic detergent (e.g. alkyl benzene sulphonate, alkyl sulphate, alkyl sulphonate or alkyl ether sulphate) and/or nonionic detergent is added in an amount from 2% to 15% by weight of the composition.

#### Additional Components

An optional but preferred component of the present compositions is a polycarboxylate material selected to interact with the precipitated inorganic phosphate solids to minimise their entrapment by and deposition on the fabrics. Although the mechanism of this interaction is not fully understood it is postulated that the polymers modify the aggregation characteristics of the precipitated inorganic salts and also interfere with the deposition of the latter by bonding to the fabric surface and tending to repulse the suspended inorganic salts. Typical polycarboxylate materials are described in German Offenlegenschrift 2,650,281.

One group of polycarboxylate materials found to be of value in the present invention comprises homopolymers having a repeating unit of formula



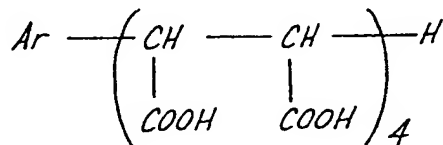
where  $R_1$  is H or OH,  $R_2$  is H or  $-COOH$ .

This group of polycarboxylates include polyacrylic, polymaleic and polyhydroxyacrylic acids. Polymers having a molecular weight in the range 500—250,000 are satisfactory, but a preferred range of molecular weight is 500 to 50,000, more preferably 500—30,000.

A preferred example of this group of polycarboxylates is a polyhydroxyacrylic acid having a molecular weight of approximately 25,000 and available from Solvay et Cie S.A.

A second group of polycarboxylate materials comprises copolymers of maleic acid with an olefinic monomer such as ethylene, styrene or vinyl methyl ether. The ratio of the number of units of maleic acid to those of the other monomer should be in the range from 1:1 to 1:2 and the molecular weight can be from 500—250,000, preferably from 500—50,000, more preferably from 500—10,000. Preferred examples of this group of polycarboxylates are the styrene-maleic acid copolymers available from the Arco Chemical Co. under the designations SMA 1000A and SMA 2000A, these copolymers each having a molecular weight of approximately 2,000 and comprising styrene: maleic acid ratios of 1:1 and 2:1 respectively.

A further group of polycarboxylate materials is made up of oligomers of maleic acid and an aromatic molecule such as toluene or xylene. These oligomers have the formula



and a highly preferred material is a xylene-maleic acid oligomer available from Ciba-Geigy under the designation PC 136.

The polycarboxylate materials are preferably used in the form of their alkali metal, especially sodium salts, and the level of usage of these polycarboxylate materials, calculated as the sodium salts, in the compositions of the invention is from 0.1% to 10% by weight of the composition, preferably from 0.3% to 5% and most preferably from 0.5% to 3% by weight.

A further optional component of compositions of the present invention is a finely divided material serving as a nucleation site or crystallisation promoter for the ortho- and pyrophosphates precipitated by the mineral hardness present in the wash liquor and arising from the soiled fabrics. In order to be effective as a nucleation site, a material must be crystalline and have a configuration compatible with the precipitating species, in addition to being itself of small particle size. Suitable materials for this purpose are dicalcium pyrophosphate, calcium orthophosphate, magnesium silicate, polystyrene and cellulose phosphate, calcium pyrophosphate and magnesium silicate being most preferred. The particle size of such nucleation site materials should not exceed  $4\mu$  and should preferably be less than  $0.5\mu$ . Measurement of particle sizes in this range can be achieved by making an electron micrograph of a sample of the material and then counting the particles with the aid of a Zeiss counter. An alternative technique is to measure the rate of sedimentation of a sample in water.

As disclosed in German Offenlegungsschrift 2,650,281, the granular or other particulate compositions of the invention preferably incorporate from 0.5 to 6%, more preferably from 1 to 5% by weight of the final composition, of a particulate, e.g. crystalline, water soluble magnesium salt (calculated as  $MgSO_4$ ). Preferably the salt is magnesium chloride or magnesium sulphate and can be in the form of their hydrates. The magnesium salt should be dry mixed. Apparently it is desirable that it should not react to a considerable degree with the other components of the composition before it is dissolved in water in a wash liquor, and if necessary, the

magnesium salt may be coated or otherwise protected from premature reaction with the rest of the composition.

5 The composition of the invention can, of course be supplemented by other normal components of detergent compositions. These components include bleaching agents, such as sodium perborate or percarbonate and organic peroxy compounds and chlorine bleaches; enzymes, activators and stabilisers for bleaches or enzymes; soil suspending or soil release agents, such as sodium carboxymethyl and other cellulose derivatives and polyethyleneglycols; suds controlling agents such as the ester capped nonionic materials described in Belgium Patent 834,479, 10 the wax suds depressants described in Belgian Patent No. 824,295, the silicone suds controlling agents disclosed in British Patent 1,407,997 and in Belgium Patent 847,268 and fatty acids comprising an average from 18 to 24 carbon atoms, e.g. hydrogenated fish oil; tarnish inhibitors; organic solvents; hydrotopes (especially in liquid products) such as the lower mono- and poly- alkyl benzene and naphthalene sulphonates; colouring matters and perfumes. 15

A valuable optional ingredient of the present compositions consists of particulate smectite clay materials, namely sodium and calcium montmorillonites, sodium saponites, and sodium hectorites. Mixtures of these clays can be used. These smectite clays are present in the built detergent compositions of the 20 invention, in an amount from 1% to 50%, preferably from 5% to 25% by weight. The clays used herein are "impalpable", i.e. have a particle size which cannot be perceived tactilely. Impalpable clays have particle sizes below 50 microns; the clays used herein have a particle size range of from 5 microns to 50 microns. 25

The clay minerals can be described as expandable, three-layer clays, i.e. aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay and preferably at least 60 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites. 30

The clay minerals are described in detail in British Patent 1,400,898. A preferred method of addition to the instant detergent compositions is by agglomerating with the antistatic/dispersion inhibitor combination described earlier using a suitable agglomerating aid, for example an aqueous solution of disodium pyrophosphate. The clay can also be agglomerated by itself and 35 separately added to the instant detergent compositions.



## EXAMPLES 1 to 3

The following built granular detergent compositions were prepared:

		Examples			Standard		
		1	2	3	1	2	
5	Sodium linear dodecyl benzene sulphonate	8.0	8.0	7.28	8.0	8.0	5
10	Tallow alcohol condensed with 11 moles of ethylene oxide	0.5	0.5	0.5	1.7	1.7	10
	C <sub>18-22</sub> fatty acids	—	—	—	3.45	3.45	
	90/10 Tallow soap/Coconut Soap	—	—	9.1	—	—	
15	Sodium orthophosphate	10.0	10.0	9.1	—	10.0	15
	Sodium pyrophosphate	6.0	6.0	5.46	—	6.0	
20	Sodium tripolyphosphate	—	—	—	31.7	—	20
	Sodium silicate (2.0 mole ratio)	10.0	10.0	9.1	6.1	10.0	
	Sodium polyhydroxyacrylate <sup>1</sup>	—	1.5	1.36	—	—	
25	Sodium sulphate	4.46	6.09	5.44	8.03	22.5	25
	Sodium carboxymethylcellulose	0.47	0.47	0.47	0.84	0.46	
	Tetra sodium ethylenediamine tetraacetate	0.21	0.21	0.19	0.21	0.21	
30	Brightener	0.23	0.23	0.21	0.23	0.23	30
	Moisture	7.0	7.87	7.05	7.03	5.0	
	Spray Dried Granules	46.87	50.87	55.26	67.26	67.55	
35	Sodium perborate tetrahydrate	32.0	32.0	29.12	32.04	32.0	35
	Enzyme	0.3	0.3	0.27	0.3	0.3	
	Cationic agglomerate <sup>2</sup>	16.40	16.4	14.92	—	—	
40	Magnesium sulphate	4.0	—	—	—	—	40
	Polyethylene glycol 400	0.25	0.25	0.25	0.25	—	
	Perfume	0.18	0.18	0.18	0.15	0.15	
	Total	100.00	100.00	100.00	100.00	100.00	
45	Notes:						45
	1. Sodium polyhydroxyacrylic acid marketed as PHAS by Solvay & Cie.						
	2. Softener agglomerate has the following weight percentage composition:						
	Ditallowdimethylammonium chloride				25.6		
	Tallow alcohol				8.5		
50	Sodium montmorillonite clay				48.8		50
	Disodium pyrophosphate				2.6		
	Water				14.5		
					100.0		

The agglomerate was prepared from prills of ditallowdimethyl ammonium chloride and tallow alcohols, by agglomerating with montmorillonite clay using a 15 weight% aqueous solution of disodium pyrophosphate as agglomerating aid.

5 In a typical test, fabric softness measurements were obtained on swatches of terry towelling (6 replicates) washed in 1% by weight solutions of the test products in a Minidrum washing machine. The solutions were prepared in 18°H water and washed at 95°C. for 50—60 minutes, rinsed and then line-dried. The washed and dried swatches were compared for softness by a panel of four judges using a 9 point Scheffe scale. In such a test, the compositions of Examples 1 to 3 were found to give significant softening benefits in comparison with the standard compositions. 10 Moreover, the addition of quaternary ammonium salt was found to have no detrimental effort on fabric ash deposition performance and the resulting formulations gave a level of cleaning performance comparable to a standard tripolyphosphate built composition (viz. Standard I).

15 Products with similar performance are obtained when the sodium alkyl benzene sulphonate is replaced by C<sub>10-22</sub> olefine sulphonates, C<sub>10-22</sub> paraffin sulphonates, and by zwitterionic detergents such as C<sub>10-18</sub> alkyl dimethyl ammonium propane sulphonate or hydroxypropane sulphonate.

Enhanced performance is also obtained when sodium polyhydroxyacrylate is replaced by, as their sodium salts, a copolymer of maleic anhydride and vinyl methyl ether having a molecular weight of about 240,000 a copolymer of methyl methacrylate and maleic acid, the molar ratio of the monomers being about 1:1, of molecular weight about 10,000; an ethylene-maleic acid copolymer of molecular weight about 4,000; a propylene-maleic acid copolymer of molecular weight about 30,000; 1-hexene-maleic acid copolymer of molecular weight about 25,000; a vinyl pyrrolidone-maleic acid copolymer of molecular weight about 26,000; a styrene-maleic acid copolymer of molecular weight about 20,000; a 1:3 copolymer of acrylic acid and itaconic acid; a 1:4 copolymer of 3-butenic acid and methylene-malonic acid; a 1:9 copolymer of isocrotonic acid and citraconic acid; a 1:1.9 copolymer of methacrylic acid and aconitic acid; and a 1.2:1 copolymer of 4-pentenoic acid and itaconic acid. 20 25 30

Enhanced performance is also obtained when ditallowdimethyl ammonium chloride is substituted on an equal weight basis by dodecylmethylmorpholinium acetate, and ditallowdimethylammonium methylsulfate, methyl (1) stearylaimidoethyl (2) stearylimidazolinium methosulfate or methyl (1) stearylaimidoethyl (2) stearylimidazolinium chloride. 35

## EXAMPLES 4 to 9

Granular detergent compositions were prepared having the following compositions:

		4	5	6	7	8	9	
5	Sodium linear dodecyl benzene sulphonate	8.0	8.0	8.0	8.0	1.0	7.0	5
	Sodium tallow alkyl sulphate	1.0	12.0	1.0	—	—	—	
	Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O 3.2:1)	6.1	6.0	6.1	6.1	6.1	6.1	
10	Dobanol 45-7 (4)	—	—	—	3.0	8.0	4.0	10
	Sodium sulphate	5.2	31.4	8.2	9.2	12.0	16.6	
	Dobanol 45-4 (5)	—	—	—	—	4.0	—	
	Disodium orthophosphate	7.5	15.0	6.5	11.0	3.0	5.0	
15	Sodium coconut soap	5.0	—	—	—	12.0	—	15
	Tetrasodium pyrophosphate	7.1	5.0	6.0	3.0	10.0	15.0	
	Pentasodium tripolyphosphate	5.0	—	4.0	2.0	—	—	
20	Sodium perborate tetrahydrate	32.0	—	32.0	32.0	15.0	30.0	20
	Sodium carboxymethyl cellulose	0.8	1.0	0.8	0.8	0.8	0.8	
	Silicone prills (1)	2.0	2.0	2.0	2.0	—	2.0	
25	Tallow alcohol (EO) <sub>11</sub>	0.5	—	0.5	0.5	—	0.5	25
	Microcrystalline wax (2)	0.3	0.6	0.3	0.3	—	—	
	Gantrez AN119 (3)	1.2	1.0	1.3	1.0	—	1.0	
	Cationic Agglomerate (7)	10.0	12.0	15.0	16.0	20.0	5.0	
30	Enzyme (6)	0.3	—	0.3	—	—	—	30
	Water and miscellaneous	to 100						

## Notes:

- (1) Comprising 0.14 parts by weight of an 85:15 by weight mixture of silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 25 molar proportions of ethylene oxide.
- (2) Witcodur 272 M. pt. 83°C, (Trade name)
- (3) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 240,000 marketed by GAF. This was prehydrolysed with NaOH before addition.
- (4) Trade name: primary C<sub>14-15</sub> alcohols condensed with 7 molar proportions of ethylene oxide, marketed by Shell.
- (5) Trade name: primary C<sub>14-15</sub> alcohols condensed with 4 molar proportions of ethylene oxide, marketed by Shell.
- (6) Maxatase (trade mark): 15% pure enzyme marketed by Gist-Brocades.
- (7) See Examples I to III.

The above compositions, employed at a concentration of 0.12% by weight, provide simultaneous cleansing, softening and antistatic effects at low builder phosphorus levels when employed in the washing cycle of a conventional home laundering process.

## EXAMPLES 10 to 12

Through-the-wash softening compositions were prepared with the following compositions

		10	11	12	
5	Sodium alkyl benzene sulfonate having from 10 to 14 carbon atoms in the alkyl group	16.00	16.00	16.00	5
10	Mixture of fatty acids with chain lengths of from 14 to 22 carbon atoms	2.36	2.36	2.36	10
	Tallow fatty alcohol (hardened) condensed with 11 moles of ethylene oxide per mole of fatty alcohol	1.60	1.60	1.60	
15	Sodium orthophosphate	10.0	6.0	15.0	
	Sodium pyrophosphate	6.0	10.0	5.0	15
	NaCl	6.0	6.0	6.0	
	Sodium perborate tetrahydrate	30.0	15.0	10.0	
	Sodium carboxymethyl cellulose (70% active)	1.0	1.0	1.0	
20	Na <sub>2</sub> SO <sub>4</sub>	18.43	21.43	20.96	20
	Proteolytic enzyme (1)	0.24	0.24	0.24	
	Brightener	0.13	0.13	0.13	
	Perfume	0.18	0.18	0.18	
	Moisture	4.50	4.50	4.50	
25	Gelwhite GP—powdered sodium montmorillonite clay having an ion exchange capacity of 100 meq/ 100 gm.	—	10.0	10.0	25
30	Distearyl dimethyl ammonium chloride (2)	1.0	2.0	5.0	30
	Tallow fatty alcohol (hardened) condensed with 25 moles of ethylene oxide per mole of fatty alcohol	1.0	—	0.64	
	Miscellaneous	—	to 100	—	
35	Note:				35
	(1) The enzyme was dry-mixed with the rest of the formulation in each instance.				
	(2) The quaternary used is AROSURF TA-100, a product of Ashland Chemicals.				
40	The above compositions, employed at a concentration of 0.12% by weight, provide simultaneous cleansing, softening and antistatic effects at low builder phosphorus levels when employed in the washing cycle of a conventional home laundry process.				40

## EXAMPLES 13 to 14

45	Heavy duty liquid detergent formulations comprise			45
		13	14	
	Potassium dodecyl benzene sulphonate	20	20	
50	Dobanol 45-7 (1)	—	10	
	Dipotassium orthophosphate	10	6	50
	Tetrapotassium pyrophosphate	6	10	
	Gantrez AN119 (1)	1	1	
	Sodium toluene sulphonate	6	6	
	Ethanol	—	10	
55	Cationic Agglomerate (2)	8	4	55
	Water and miscellaneous	—	to 100	

Notes:

(1) See Examples 4 to 9.

(2) Prills of ditallowdimethylammonium chloride and tallow alcohol (3:1  
weight ratio).

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## WHAT WE CLAIM IS:—

1. A built detergent composition comprising by weight:

(a) from 1% to 70% of an organic surfactant selected from anionic, nonionic and zwitterionic surfactants, and mixtures thereof,

(b) from 5% to 50% of a mixture of water soluble ortho and pyrophosphate salts, the weight ratio of ortho- to pyrophosphate salts being in the range from 9:2 to 3:7,

(c) from 0.5% to 25% of one or more quaternary ammonium compounds of formula  $(R_1R_2R_3R_4N)^+Y^-$ , wherein at least one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is an organic radical containing a group selected from a  $C_{18}$ — $C_{22}$  aliphatic radical, or an alkyl phenyl or alkyl benzyl radical having 10 to 16 carbon atoms in the alkyl chain, the remaining group or groups being selected from  $C_1$ — $C_4$  alkyl,  $C_2$ — $C_4$  hydroxyalkyl, and cyclic structures in which the nitrogen atom forms part of the ring, and Y constitutes an anionic radical.

2. A detergent composition according to Claim 1, wherein the quaternary ammonium compound is selected from ditallow dimethyl ammonium chloride and ditallow dimethyl ammonium methyl sulphate.

3. A detergent according to Claim 1 or 2, comprising from 1% to 25% by weight of a particulate combination comprising an intimate mixture consisting essentially of:

A. 80% to 20% by weight of the particulate combination of said quaternary ammonium compound and

B. 20% to 80% by weight of the particulate combination of a dispersion inhibitor, being a solid organic material having a solubility in water of 50 ppm max at 25°C and a softening point in the range 100°F to 200°F, said material being selected from the group consisting of paraffinic waxes, cyclic and acyclic mono- and polyhydric alcohols, substituted and unsubstituted aliphatic carboxylic acids, esters of the foregoing alcohols and acids,  $C_3$ — $C_4$  alkylene oxide condensates of any of the foregoing materials and mixtures thereof, substantially all of the individual particles having a size within the range 10 $\mu$  to 500 $\mu$ , said product having a solubility in water of 50 ppm max at 25°C and having a softening point in the range 100°F to 200°F.

4. A detergent composition according to Claim 3, wherein the weight ratio of quaternary ammonium compound to dispersion inhibitor lies in the range of 1:1 to 4:1.

5. A detergent composition according to Claim 4, wherein the weight ratio of quaternary ammonium compound to dispersion inhibitor lies in the range of 3:2 to 7:2.

6. A detergent composition according to any of Claims 3 to 5, wherein the intimate mixture is formed of a solidified comelt of the quaternary ammonium compound and the dispersion inhibitor.

7. A detergent composition according to any of Claims 3 to 6 wherein the dispersion inhibitor is selected from tallow alcohol and castorwax.

8. A detergent composition according to any preceding Claim, wherein the weight ratio of orthophosphate to pyrophosphate is in the range from 7:3 to 1:1.

9. A detergent composition according to Claim 8, wherein the weight ratio of orthophosphate to pyrophosphate is in the range from 65:35 to 55:45.

10. A detergent composition according to any preceding claim, wherein the combined proportion of said ortho- and pyrophosphates is from 10% to 35% by weight of the composition.

11. A detergent composition according to Claim 10, wherein said combined proportion is from 15% to 33% by weight of the composition.

12. A detergent composition according to any preceding Claim, comprising from 1% to 20% by weight of a  $C_8$  to  $C_{24}$  fatty acid salt.

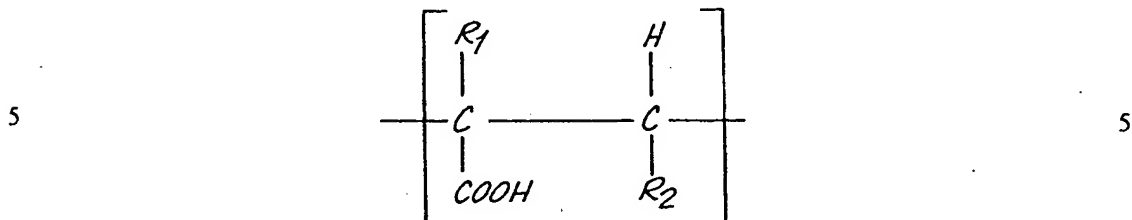
13. A detergent composition according to any preceding Claim, wherein the quaternary ammonium compound and the  $C_8$  to  $C_{24}$  fatty acid salt are present in a weight ratio from 20:1 to 1:30.

14. A detergent composition according to Claim 12, wherein the quaternary ammonium compound and the  $C_8$  to  $C_{24}$  fatty acid salt are present in a weight ratio of from 5:1 to 1:10.

15. A detergent composition according to Claim 13, wherein the quaternary ammonium compound and the  $C_8$  to  $C_{24}$  fatty acid salt are present in a weight ratio of from 1:1 to 1:5.

16. A detergent composition according to any preceding claim comprising from 0.1% to 10% by weight (calculated as the sodium salt) of a polycarboxylate material selected from the group consisting of:

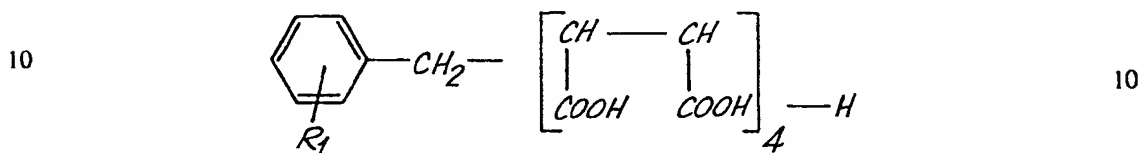
(i) homopolymers of molecular weight 500—250,000 having a unit of formula



wherein  $R_1$  is H or OH,  $R_2$  is H or  $-COOH$ .

(ii) copolymers of maleic acid with respectively ethylene, vinyl methyl ether and styrene of molecular weight 500—250,000 and

(iii) an aryl-maleic acid oligomer of formula



where  $R_1$  is H or  $\text{CH}_3$ .

17. A detergent composition according to any preceding claim, wherein the polycarboxylate material is polyhydroxy acrylic acid or an alkali metal salt thereof.

18. A detergent composition according to any preceding claim, comprising a water soluble nucleation promoter having a particle size not greater than  $4\mu$ .

19. A detergent composition according to Claim 18, wherein the nucleation promoter is selected from calcium pyrophosphate, calcium orthophosphate, magnesium silicate, polystyrene and cellulose phosphate.

20. A detergent composition according to any preceding claim, such that its pH in-use is in the range from 9.0 to 10.5.

21. A detergent composition according to any preceding claim in granular form.

22. A detergent composition according to any preceding Claim comprising from 5% to 25% by weight of clay selected from the group consisting of sodium and calcium montmorillonites, sodium saponites, sodium hectorites and mixtures thereof, said clay having an average particle size in the range from 5 to 50 microns.

23. A detergent composition substantially as described hereinbefore with reference to any one of the examples.

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